Refinements to the MARTHE model to enable the simulation of the fate of agricultural contaminants from the soil surface to and in groundwater.

Dominique Thiéry, Catherine Golaz, Alexis Gutierrez, Wieslaw Fialkiewicz, Coralie Darsy, Christophe Mouvet, Igor G. Dubus

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D. Thiéry, C. Golaz, A. Gutierrez, W. Fialkiewicz, C. Darsy, C. Mouvet, **I.G. Dubus**

BRGM, Water Department, Orléans – France.

Corresponding author: BRGM - Avenue C. Guillemin - BP 6009 - 45060 Orléans Cedex 2 - France. Tel: +33 2 38 64 47 50 - fax: +33 2 38 64 34 46 - E-mail: i.dubus@brgm.fr

Abstract

MARTHE (Modelling Aquifers with an irregular Rectangular grid, Transport, Hydrodynamics and Exchanges) is a versatile 3D groundwater model designed to enable the hydrodynamic and hydro-dispersive modelling of groundwater flow in hydrosystems. Refinements to the model were made as part of the European project PEGASE to allow the simulation of pesticide fate in the soil. New descriptions for cropping and pesticide sorption and degradation were added to the model. The verification exercise undertaken using analytical solutions published in the literature (sorption, degradation) and experimental data (cropping, degradation) demonstrated that the new code added to MARTHE has been correctly implemented in the model. In addition, the close fits obtained between predicted and theoretical/measured data confirmed the sound numerics of the model. These refinements and their testing mean that the model can now be used with confidence to simulate the fate of pesticides from the soil surface to and in the groundwater. The model is expected to be a useful tool in the modelling of pesticide fate through the whole continuum root zone – unsaturated zone – saturated zone, in 1, 2 or 3 dimensions. In particular, the model may be used to i) assess the risk of pesticide leaching to groundwater resources at a range of scales; ii) provide explanations for detection / non-detection of pesticides in monitoring programmes; and, iii) manage inputs of pesticide to a particular area within a context of sustainability of groundwater resources.

Keywords

Model, verification, soil, unsaturated zone, saturated zone, pesticide

1. Introduction

Most pesticide leaching models used to assess the risk of compounds being transferred to groundwater resources within the context of pesticide registration or research on pesticide fate include a detailed description of processes affecting pesticide fate in the soil, but their remit is limited to 1D simulation in the first few metres of soil. Transport and reactive processes occurring in the deeper unsaturated and saturated zones are ignored. Conversely, deterministic groundwater models (e.g. MODFLOW, SUTRA) usually do not allow the simulation of the fate of pesticides at the soil-atmosphere boundary and in soil, where attenuation processes key to the overall fate of pesticides occur. The present paper reports on the refinement of the 3D groundwater model MARTHE to allow the simulation of pesticide fate from the soil surface to and in groundwater. A rigorous verification exercise to ensure that the new code was correctly implemented was undertaken.

2. The MARTHE model

MARTHE (Modelling Aquifers with an irregular Rectangular grid, Transport, Hydrodynamics and Exchanges) is a versatile 3D groundwater model designed to enable the hydrodynamic and hydro-dispersive modelling of groundwater flow in hydrosystems (Thiéry D., 1990, 1993, 1994, 1995; Thiéry D. & Golaz C., 2002). Hydrodynamic calculations are based on a fully implicit scheme with a 3D finite volumes discretization. The system simulated may be represented with a classical confined/unconfined scheme or by a unsaturated zone – saturated zone continuum. In this latter case Richards' equation is solved with retention and relative hydraulic conductivity relations selected from a number of formulations (Van Genuchten, Brusaert, Brooks and Corey, Gardner, homographic, power law etc.). Advective, diffusive and dispersive transport can be simulated using three different techniques (donor cell, total variation diminishing, method of characteristics using particles) depending on the situation considered (predominance of convection or dispersion). Calculations for energy, temperature, mass and water fluxes are simultaneously fully coupled within the model. Interactions with the atmosphere (rainfall, potential evapotranspiration) may be integrated through coupling to hydroclimatic balance models which compute actual evapotranspiration, infiltration and runoff. The aquifer system may be coupled to a river or a drain network which receives runoff and exchanges flow along the reaches. The horizontal discretisation uses an irregular rectangular grid which may integrate nested grids in zones of particular interest or near singularities. The vertical discretisation may be represented as a fully 3D system or a complex multilayer system with possibilities of disappearing layers and short circuits. MARTHE integrates pre- and post-processors to facilitate the preparation, management and graphical processing of input data and modelling results. The system also allows imports/exports to be made with the GIS software MapInfo and integrates its own tool for interpolation of scattered data.

MARTHE has been applied to over 200 aquifer systems since its first release in the late 1980's. Fields of application have included i) the management of groundwater resources (e.g. water balance assessments, evaluation of the potential impacts of abstractions); ii) civil engineering and mining work (e.g. impact of underground activities); and, iii) environmental assessments (both point and diffuse pollution). The scale of applications of the model has ranged from detailed investigations into water movement in soil (soil volumes of a few cm with cells of a few mm) to simulation of large multilayer aquifer systems (150,000 km^2, 1,500-m thickness). The temporal scale of application ranged from seconds to 15,000 years for long-term geochemical predictions.

3. Addition of new functionalities enabling the simulation of the transfer of water and pesticides in the root zone – unsaturated zone – saturated zone continuum

MARTHE was initially designed as a 3D groundwater model for water transport in groundwater. Although the remits of the model have largely broaden since the early versions of the model (e.g. through simulation of fluxes in the unsaturated zone and of solute transport or the possibility to couple MARTHE to stand-alone (geo)chemical models), the model was found in 2000 to be unsuitable for adequately simulating the fate of pesticides from the soil surface to and in groundwater. Also, MARTHE was implementing a simplified description of the water balance at the upper boundary and descriptions of physical and biological processes known to drive the overall fate of pesticides (sorption, degradation) were not included in the model. MARTHE was therefore adapted as part of the European project PEGASE (Mouvet C. et al., 2004) through the addition of new code for cropping and pesticide sorption and degradation.

New functionalities for cropping

The presence of vegetation significantly influences water and pesticide fluxes in soil through i) plant transpiration; and, ii) plant uptake of water and solutes. The following features were implemented in MARTHE to improve water and pesticide fluxes close to the soil surface: i) breakdown of evapotranspiration into soil evaporation and transpiration by vegetation; ii) water uptake by vegetation over a variable depth that depends on the condition of root development and vertical root distribution; iii) restriction of water uptake according to the state of hydric stress experienced by vegetation; and, iv) pesticide uptake through the root system, depending on the product considered.

New functionalities for pesticide sorption

The schemes selected for description of sorption for pesticides were those of Langmuir and Freundlich.

The Langmuir sorption isotherm expressing the relation between the solid phase concentration S_M and liquid phase concentration C at equilibrium is given as:

$$S_M = Q \cdot \frac{K_L \cdot C}{1 + K_L \cdot C}$$

where: S_M = Solid phase mass concentration [kg/kg], C = Liquid phase volumetric concentration [kg/ m^3], Q = Total sites for solid phase concentration [kg/kg] and K_L = Langmuir constant [m^3/kg]

The Freundlich sorption isotherm writes:

$S_M = K_F \, . \, C^B$

where: B = Freundlich exponent (generally < 1), K_F = Freundlich constant in unit $[m^3/kg]^B$.

New functionalities for pesticide degradation

Two types of degradation schemes were integrated in MARTHE. The first scheme is sequential (or "linear"), in that compound #1 is assumed to be degraded into compound #2, which in turn is degraded into compound #3, etc. The second scheme enables the simulation of the degradation of a compound into multiple metabolites. The current version of the model does not allow the combination of the two degradation schemes although modifications to the code will enable the simulation of complex degradation pathways using complex kinetics in the near future.

New functionalities for the effect of water content and temperature on degradation

Pesticide degradation is influenced by temperature and soil humidity conditions. A review of the different equations used to describe the effect of temperature and soil moisture variations on degradation was undertaken and supported the selection of five correction schemes for temperature (LEACHP, AGRIFLUX, MACRO, WAVE and PELMO) and six schemes for humidity (LEACHP, AGRIFLUX aerobic, AGRIFLUX anaerobic, MACRO, WAVE and PELMO).

4. Verification exercise

Cropping

New subroutines for crop development were evaluated using data from the La Côte St André (Isère, France) experimental site (Normand B. et al., 1997) where water fluxes on a bare soil plot and a plot cropped with maize were monitored over three successive cropping seasons. All data supporting the evaluation were provided by B. Normand (LTHE, Grenoble, France). Figure 1 presents measured and simulated water contents for the two plots.

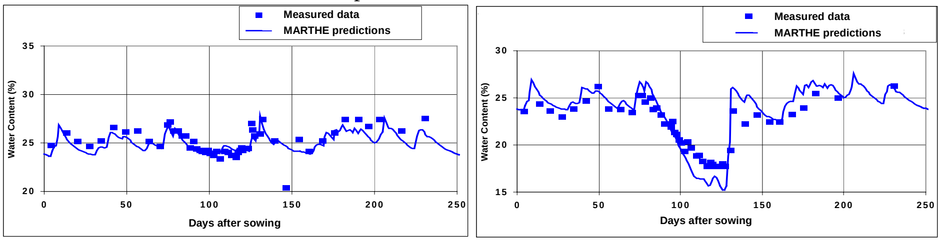

Figure 1. Observed (symbols) and simulated (line) water contents at La Côte Saint André in 1992 (left: bare soil; right: maize)

Sorption

The correct implementation of the Langmuir and Freundlich equations were tested against solutions provided by Zheng C. et al. (1998) and Huang K. et al. (1998), respectively (Figure 2).

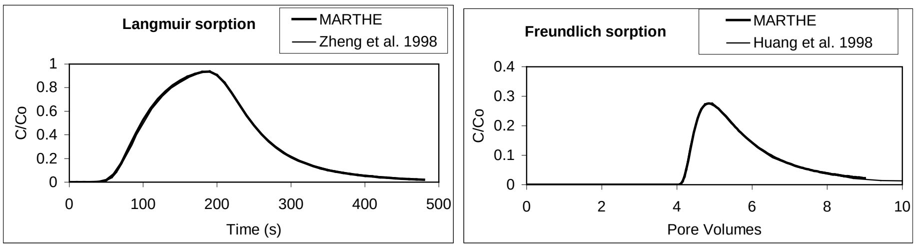

Figure 2. Comparison of MARTHE predictions with those of Zheng et al. (1998) (Langmuir; left) and of Huang et al. (1998) (Freundlich; right). Thick line = MARTHE; Slim line = reference. The two lines are superimposed in the Figure.

Degradation schemes

The correct implementation of degradation subroutines in the model was checked using an analytical solution from Cho C.M. (1971) using a test scenario described by Van Genuchten M.Th. (1985). The modelling considered the transport of NH_4^+, NO_2^- and NO_3^- ($NH_4^+ \rightarrow NO_2^- \rightarrow NO_3^-$) in a horizontal column which received an input of NH_4+ at its left boundary (Figure 3).

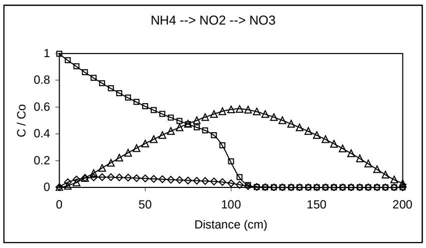

Figure 3. Comparison of MARTHE predictions (lines) with analytical calculations (symbols) obtained using the CHAIN code from Van Genuchten. (squares: NH_4^+; diamonds: NO_2^-; triangles: NO_3^-)

Effect of temperature and humidity variations on pesticide degradation
A number of simulations based on the description of the leaching of bentazone in a 2-m deep Dutch soil (Vredepeel dataset; Boesten J.J.T.I., 2000) were carried out to demonstrate the effects of humidity and temperature corrections on model predictions (Figure 4).

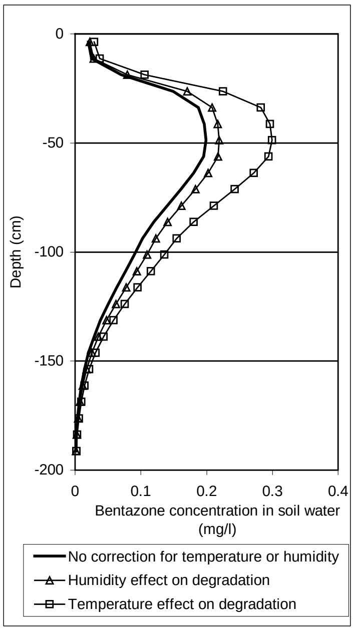

Figure 4. Influence on MARTHE predictions for concentrations of bentazone in the Vredepeel soil profile of the effects of temperature and saturation corrections of degradation

5. Conclusions

The verification exercise undertaken using analytical solutions published in the literature (sorption, degradation) and experimental data (cropping, degradation) demonstrated that the new code added to MARTHE has been correctly implemented in the model. In addition, the close fits obtained between predicted and theoretical/measured data confirmed the sound numerics of the model. These refinements and their testing mean that that model can now be used with confidence to simulate the fate of pesticides from the soil surface to and in the groundwater. The model is expected to be a useful tool in the modelling of pesticide fate through the whole continuum root zone – unsaturated zone – saturated zone, in 1, 2 or 3 dimensions. In particular, the model may be used to i) assess the risk of pesticide leaching to groundwater resources at a range of scales; ii) provide explanations for detection / non-detection of pesticides in monitoring programmes; and, iii) manage inputs of pesticide to a particular area within a context of sustainability of groundwater resources.

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